Phase Transition and Debye-Waller Factor of KDP

H. Mashiyama, T. Asahi, H. Kasano and T. Miyoshi
Faculty of Science, Yamaguchi University

The mechanism of the phase transition in KDP (KH_2PO_4) has been interested widely. The isotope effect could be explained by the famous proton tunneling model[1] for long years. But the replacing proton by deuteron changes atomic distance, which could also present the characteristic isotope effect.[2]

With using neutron diffractometry, detailed structural studies were performed in a quarter century ago, and the order-disorder picture of proton distribution was revealed.[3] However, the analysis was limited above 127K, so the temperature range should be expanded to discuss the proton motion definitely.

A single crystal of KDP was set in a cryostat mounted on a diffractometer (FONDER) installed at JRR3M reactor in JARERI, Tokai.

First sample was used in the paraelectric phase P (tetragonal I-42d). In the ferroelectric phase F (orthorhombic Fdd2), dc bias field was applied to make the second sample single. Diffraction data up to 2theta<156 (neutron wave length 1.2452A) were collected at two and four temperatures in phase P and F, respectively. Absorption and extinction correction was performed by using RADIEL. Atomic parameters were refined by least-squared calculations. Nuclear density was estimated by PRIMA and visualized by VEND.[4]

Figure shows the nuclear density images at 150K. The elongated ellipsoids indicate the disordered protons. In the phase F below 122K, the proton distribution is ordered and atoms move along the z-axis with a deformation of PO_4 tetrahedrons. The temperature dependence of the Debye-Waller factor U's is plotted in Figure. The split atom method is applied for protons in the tetragonal phase, where the factor becomes smaller than the phase F. Our results are consistent with the previous one.[3] However, since the samples were different, the direct comparison between the phase P and F should be reserved currently.

The values of U at T=0 indicate that nucleus have a finite width corresponding to their wave functions. The detailed analysis will predict the local potential in which each atom is constrained.

References

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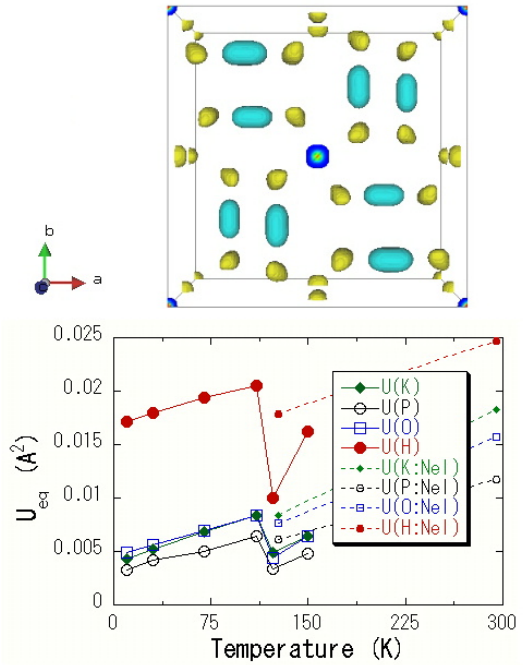

Fig. 1. Nuclear density at 150K in the tetragonal phase (top) and the temperature dependence of the thermal parameters (bottom). In the bottom, the previous results after ref. 3 are shown by broken lines.